Tyco Laboratories, Inc.
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THICK FILM SILICON GROWTH TECHNIQUES

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H. E. Bates
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A. I. Mlavsky
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Eighth Quarterly Progress Report

Subcontract No. 953365

Covering Period: 1 December 1973 - 28 February 1974

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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ABSTRACT

One inch wide silicon ribbons up to 14 inches long have been produced from graphite dies. Several different techniques have been employed to improve the semiconductor purity of our silicon. This has resulted in a general increase in quality although the techniques involved have not been optimized. The power factor of uncoated ribbon solar cells produced for material evaluation has increased to approximately 75% of those evaluation cells made from commercial Czochralski silicon. The present limitation is believed due to low lifetime.

Additional work has continued with new die materials; however, only composite dies of SiO_2 and C show significant potential at this time.

A new larger system has been designed and assembled. After satisfactory temperature control and gradients are attained, significant improvements in silicon quality, uniformity, and reproducibility are expected.

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I. SUMMARY

The growth of silicon ribbon from graphite dies has been continued in order to provide evaluation samples of ribbon while implementing various purification procedures in the preparation of the dies. The improvement included better cleaning procedures, vacuum baking of the dies, selection of a purer grade of graphite and more careful handling procedures. The result of this effort has been a general improvement in semiconductor quality although the procedures are still not optimized.

There was significant variation in ribbon quality from run to run as procedures were changed. Some ribbons have shown an improvement in quality with length. Evaluation solar cells made from silicon ribbon have improved power factors up to 75% of the power factor of control cells made from commercial Czochralski silicon. Further improvement in silicon ribbon cells should be attained with systematic application of state-of-the-art purification techniques.

Further improvement in silicon quality is expected when growing from larger melt volume. For this reason a system with a 3 in. diameter crucible has been designed and built. Initial growth tests are under way. This system will also provide us with the means of determining the feasibility of long term growth through graphite dies and the effects upon the ribbon quality.

New die materials are still being investigated. The refractory silicates have shown increased stability over their silicides but still dissolve up to 1% in silicon. New composite die materials and die configurations are being investigated to minimize the problems of graphite dies. Adequate testing of these dies requires a system which provides other means than capillarity to fill the die. A differential pressure system is being incorporated into the system. These developments should provide more stable, long term growth as well as better silicon quality.

II. INTRODUCTION

One primary limitation to the large-scale use of silicon solar cells in generating electric power from sunlight has been the lack of an industrially feasible process for the growth of single crystal silicon ribbons directly and continuously from the melt. Edge-defined, film-fed growth (EFG) is a process by which single crystals may be grown with their shape controlled by the outside dimensions of a die, the growth actually occurring through a thin liquid film on the top surface of the die.[1-5] The EFG method overcomes the need for refined temperature control during growth which characterized other attempts at the growth of ribbon-shape crystals. However, the process imposes stringent requirements on the nature of the die material if semiconductor quality crystals are to be grown.

Fig. 1 illustrates the application of the EFG method to the growth of a ribbon-shaped crystal. When the crucible and melt are heated to above the melting point of silicon, the liquid silicon rises to fill the feeding slot by capillary action. A silicon seed crystal is then brought into contact with the liquid silicon in the capillary seed slot. After adjustment of the melt temperature and seed withdrawal rate, the molten silicon spreads across the top of the die until the spreading of the liquid silicon is halted by the 90° change in effective contact angle at the outer perimeter. The growth of a silicon crystal ribbon from the thin liquid meniscus shown in Fig. 1 is then established. This method has been applied to the growth of ribbons, filaments, tubes, and other shapes of sapphire, barium magnesium titanate, lithium fluoride, copper-gold alloy crystals, and beta-alumina, as well as to the directional solidification of a variety of eutectic materials.

The basic features of the EFG technique can be summarized as follows:

1. It produces accurately controlled cross sections and, in particular, thin ribbons can be produced directly.

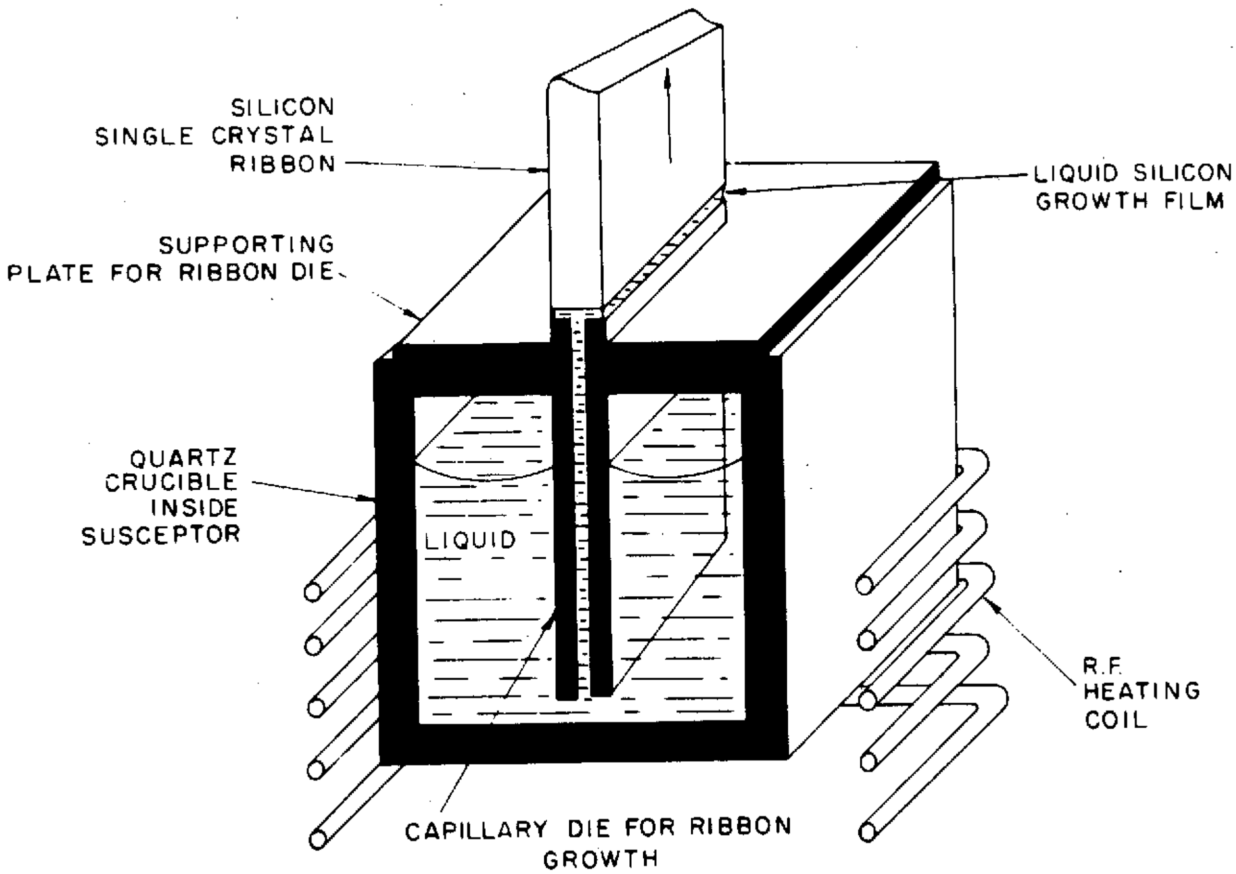

Fig. 1. Schematic drawing showing crucible and die arrangement for edge-defined, film-fed growth (EFG) of silicon ribbon

2. It is self-stabilizing over a relatively wide range of power input fluctuations by means of changes in the thickness of molten film, or meniscus.

3. Growth rates can be very fast since they are limited only by latent heat removal from the solid-liquid interface.

4. The growth interface is effectively decoupled from the bulk melt surface, permitting continuous replenishment of the melt during growth.

5. The crystal orientation can be arbitrarily chosen.

6. Because of the fast growth rate and the faster linear motion rate of the liquid supply, segregation effects tend to be completely overcome, and the crystallizing solid has the same average composition as the bulk liquid.

7. The steep thermal gradient between the growth interface and the die prevents the breakdown of planar growth. Thus, crystal perfection is enhanced and cellular substructure suppressed.

In the following sections of this report, we discuss the progress which has been made to date in applying this method to the thick film silicon ribbon growth.

III. TECHNICAL DISCUSSION

A. Ribbon Properties

During this period we have spent considerable effort in analyzing the electrical quality of our Si ribbon and correlating the results of internal and external measurements. The pertinent observations are listed below:

We have measured the resistivity of typically 0.5 to 1.5 Ω-cm P type. The mobility measured is consistent with the resistivity of the silicon. Measurements of one sample performed at the Hughes Research Laboratories show the mobility at 300°K to be 265 $cm^2/V/sec$ for a resistivity of 1.4 Ω-cm. The Hall effect versus temperature analysis indicates majority carriers to be Al at $1.5 \times 10^{16}/cc$ and B at $2.6 \times 10^{15}/cc$. The total compensating carriers were $1.2 \times 10^{15}/cc$.

Similar samples were subjected to mass spectrographic and infrared absorption analysis at the Dow Corning Research Laboratory. Mass spectrographic analysis showed significant concentrations of Al, B, Fe, Cu, C, and O. Infrared analysis shows a C concentration, between 6 and 20 ppm and the concentration of O_2 to be less than 6 ppm (detection limit). It is important to note that earlier measurements showed much greater concentrations of carbon-oxygen and other impurities. The improvement is believed to be due to better handling conditions, lower temperatures in the system, and increase in crucible diameter and charge size. In addition there was a significant difference in the impurity level of baked out and non-baked out dies. The vacuum bake out provided an order of magnitude lower concentration of Al, F, and Ca. Fe levels were reduced by a factor of 3.

Solar cell fabrication and testing in the internal Tyco and NSF program, shows the efficiency of ribbon cells to be about 3/4 that of cells made from Czochralski silicon, grown commercially or at Tyco.

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The ribbon solar cells were fabricated at Tyco with Czochralski silicon cells as controls. Fig. 2 shows an I versus V curve of these evaluation cells. They have no antireflection coating and are not optimized for material resistivities, etc.

The spectral response of ribbon cells is significant. A sharp drop-off in response is measured as the wavelength moves into red. The response to blue light, open circuit voltage, and curve factor are about the same for ribbon and standard cells. It is also noted that deeper diffusion moves the drop-off further into the red. The solar cell spectral results indicate that the bulk lifetime is limiting.

The lower lifetime is quite reasonable in view of the compensating impurities found by Hughes. Both the iron and copper identified by Dow Corning will fit into this category and both are known to be lifetime killers. The source of these impurities is expected to be the die and the crucible. The die, particularly suspect, has been made from graphite containing up to 200 ppm of Fe. There is also a significant amount of Fe in the G. E. 204 quartz - standard crucible material.

Several actions have been initiated to reduce the lifetime killing impurity concentration in the silicon ribbon.

1. A new graphite which has had the reported 200 ppm of Fe removed is being used for die.

2. The use of coolants during machining of graphite dies has been eliminated.

3. A high temperature (1250°C) treatment with HCl will be tested for removing Cu and also Fe. This will be tried on both the Si and the die.

4. The high temperature vacuum bakeout which was stopped due to undesired deposited films has been re-established after setting up a different bake-out facility.

5. The washing of glassware and source material with EDTA or other chelating agents will be tested.

6. High temperature fluorocarbon treatments will be examined to determine if they are suitable for a die cleaning procedure.

It is expected that all of these procedures will not be needed; however, it will be useful to know which combinations have the most significant effect.

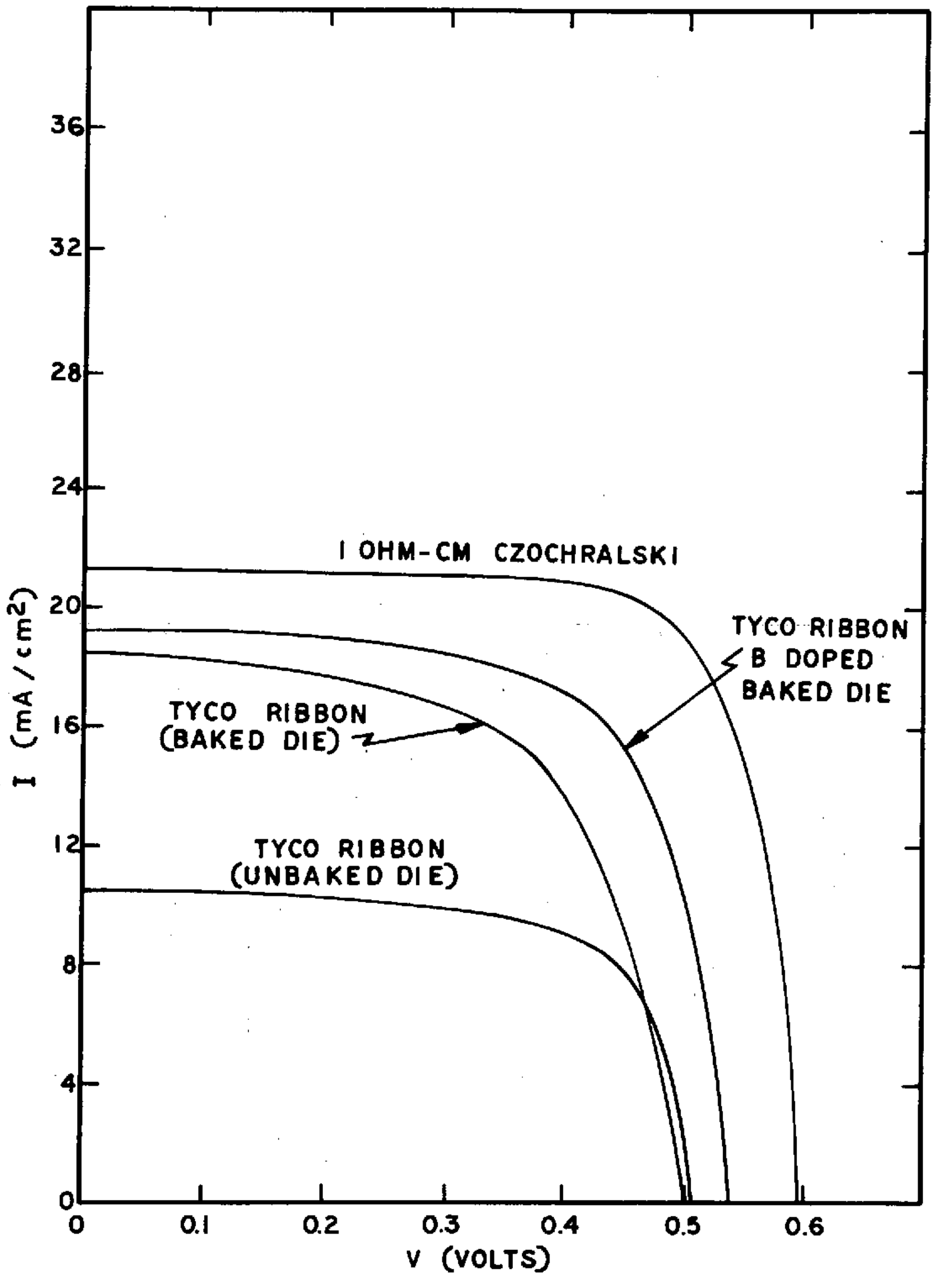

Fig. 2. Characteristic I versus V for evaluation solar cells

One of the most important steps to improve silicon quality will be the use of a system with a reasonably large melt. The present crucible is ~ 1 in. in diameter. The development of a silicon EFG system with a 3 in. diameter crucible will be discussed below.

Several other points should be mentioned, although firm conclusions cannot be reached yet. The carbon and oxygen content reported by Dow Corning is very low for ribbon grown through a graphite die and from a quartz crucible. Perhaps there is some interaction eliminating them in gaseous form (CO or CO_2).

With deeper melts, improved results may be expected with quartz die systems. In the past, some quartz and carbon dies have not even allowed the silicon to enter the capillary groove. This seems to be due to a surface effect which should disappear with larger volume and more hydrostatic pressure. In all, the wetting and movement of silicon on, over, or through another material seems to show significant hysteresis in the force required to achieve a given effect. A larger system will provide greater hydrostatic force and less interaction of the die and crucible.

Results have been obtained from items 1, 2 and 4 listed above. The improved grade of graphite, DFP-2, has been obtained and all dies are now made from this material. The die fabricators have implemented our clean handling procedures, eliminated coolants from the fabrication process, and upgraded their handling procedures.

The effectiveness of vacuum bakeout in decreasing impurities from the die in our silicon ribbon was documented by the Dow Corning analysis reported above. The older bakeout chamber had become contaminated and was abandoned for this use as it appeared to contaminate the dies with metal oxides. A new system was assembled which holds the piece to be baked out in a water cooled, double walled quartz tube. The chamber attains temperature up to 2000°C while maintaining vacuum level of 10^{-5} range. Dies have been baked out at temperatures of 1700°C, 1800°C and 1900°C. Typical baking times have been approximately one hour.

Evaluation of the resistivity of two ribbons grown from undoped melts through baked DFP-1 dies has given the results shown in Fig. 3. There is no explanation as yet, for the difference in behavior between the two runs. It is of interest to note however, that the uniform 0.8 Ω-cm of 13-341 and 0.5 Ω-cm steady-state value of 13-330 are typical of the resistivities produced hitherto by growth from DFP-1 dies both with and without vacuum firing. This could indicate that the dominant source of

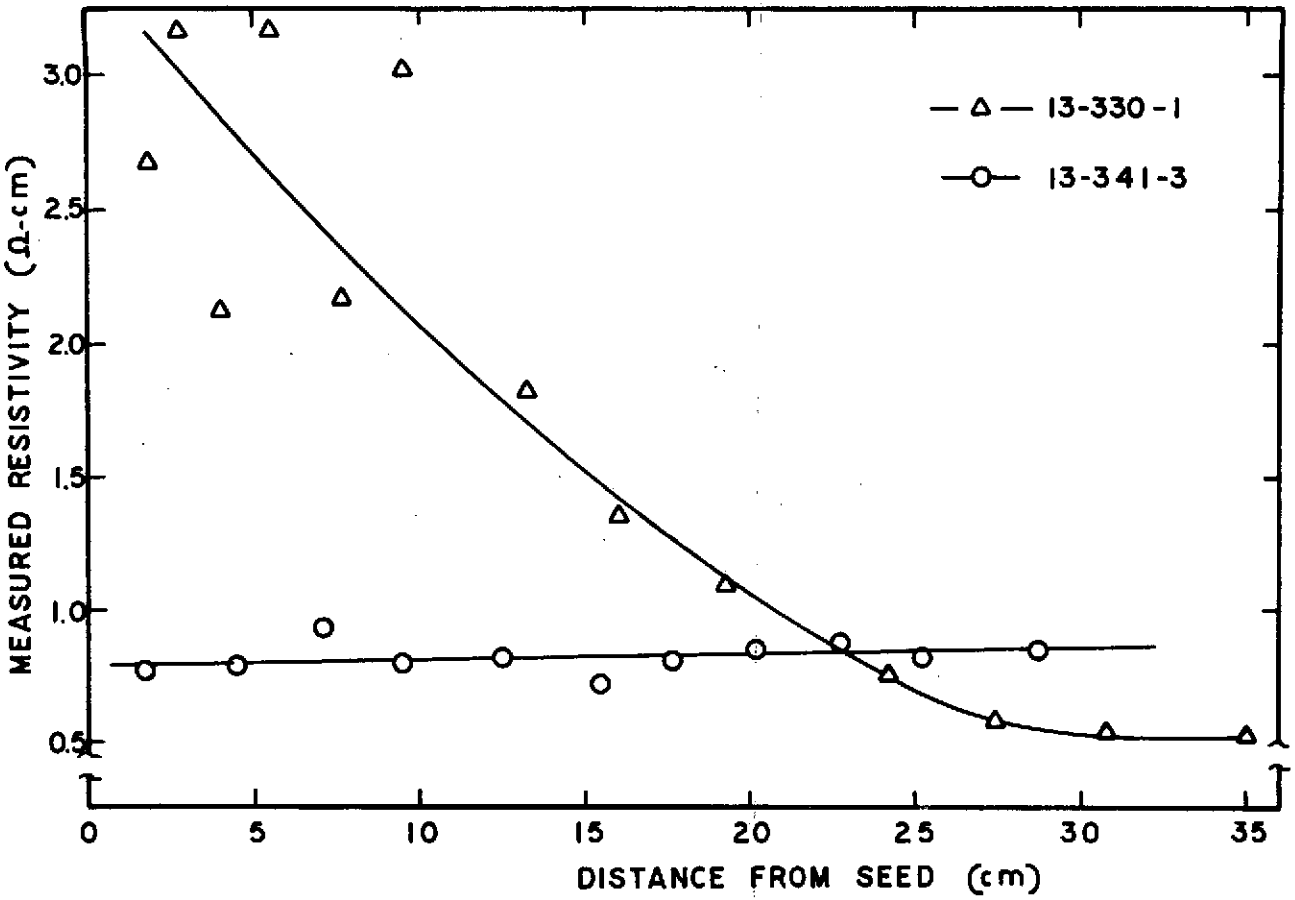

Fig. 3. Variation of resistivity with length in two ribbons grown from undoped melts through vacuum-fired graphite dies

p-type impurities is the crucible. Growth from similarly treated DFP-2 dies and undoped melts will give some further information on this point. Calculations have shown that (in this configuration) dissolution of the crucible could produce material of $\sim 1\ \Omega$-cm.

Ribbons have been grown from vacuum fired DFP-2 dies and melts doped to a nominal 2 Ω-cm using 0.1 Ω-cm boron-doped Czochralski material as a source. In two cases the resistivity of the material grown was somewhat higher than the target of 2 Ω-cm, while in two other cases the resistivity was lower by 40 to 50% than the target value. Again, the limited number of runs makes it difficult to explain the differences in behavior. Several more runs will have to be made with both doped and un-doped melts and the resulting ribbons analyzed for impurity contents in order to sort out more completely the effect of vacuum firing (and other die purifying processes) and the relative contributions of impurities from the die and the crucible.

B. System Scale-Up

If one calculates the Al input to a normal melt of 9 to 10 grams from dissolution of 25 μ of SiO_2 containing 25 ppm Al (typical of GE 204), the result is 1×10^{16} Al/cc. The 25 μ dissolution is based on an observed average over several hours; thus it may be that the initial rate is higher, accounting for most of the small discrepancy. Assuming that the above correlation of measured and calculated p-type impurity introduction is valid, it is then possible to calculate the resistivity of material grown from a larger setup. For a 3 in. diameter by 3 in. deep melt, the introduction of p-type impurities would result in about 35 to 40 Ω-cm material after one hour at temperature. We assume that there would be a corresponding reduction in impurity concentration. Doping will be used to return the resistivity to the desired level.

In light of these results, a scaled up version of the growth setup has been designed and is now operational. This system shown in the attached drawing (Fig. 2) contains a 6.0 in. O.D. furnace chamber which will take a 3.5 in. O.D. susceptor and a 3 in. O.D. $\times$ 3 in. deep crucible. With this size crucible holding a full charge, the crucible surface to volume ratio could be reduced by a factor of 5, and the melt volume will be greater by a factor of 40 for the same size die (1 in.).

The large 6 in. O.D. chamber was a source of difficulty in assembly and fabrication. One chamber broke during the water ring seal assembly. A second was returned due to the presence of pin holes. Repair resulted in strain which caused failure of the wall during initial heat up for annealing.

A third chamber is now installed and appears tight. Initial heat up of the system has produced a problem of arcing which could puncture the chamber wall. This was traced to three sources: coil design, impurities in the graphite insulation, and the pointed ends of the fibers which make up the graphite felt.

The number of turns in the coil was reduced and the diameter of the tubing making up the coil was increased to 3/8 inch. The carbon felt was baked out. This resulted in improvement but not elimination of the arcs to the wall. Therefore, a quartz tube was installed over the insulation which eliminated the problem. Another solution tried was replacement of the graphite with alumina insulation. Although this was satisfactory from the point of view of no arcing and enough insulation, the alumina tube cracked due to thermal expansion in spite of a longitudinal cut in the tubing. Changing to a selection of two thinner concentric tubes would allow alumina to be used.

A series of growth experiments with this setup has been conducted. Initially 1/4 in. thick graphite felt was wrapped around the entire setup. Also the coil was distributed with three turns on the susceptor and one on the afterheater. This provided an overheated condition within the afterheater which was melting the seed in the holder as it passed through this zone. The insulation on the afterheater was removed but it was still too hot in the afterheater and the seed was still melting above the die. Finally all four turns of the coil were placed around the susceptor. Capillary rise filled the orifice and seeding was accomplished. Attempts were made to grow but spreading of the growth was impossible indicating a need for more work on the gradient at the interface.

An inspection of the setup after disassembly showed an obvious lack of proper heating not just at the orifice but throughout the setup. The crucible had gotten so hot that it had collapsed into the molten silicon, spilling some onto the susceptor. The die had filled with silicon at the beginning of the run but when the overheating occurred it spread open on the bottom and the capillary walls were not effective in maintaining the silicon up at the orifice. Consequently, most of the silicon ran back down into the crucible leaving only a small amount at the orifice.

Temperature profiles of the setup were run and a 300° temperature difference from the bottom of the susceptor to the orifice was found. This very hot bottom probably resulted from the addition of an alumina disc placed between the susceptor and pedestal. This insulator was needed to restrict heat flow into the pulling machine which was becoming excessively hot during the initial runs.

Various coil positions and distributions were tried but the smallest differential obtained was approximately 120°C. Therefore one turn was removed and the coil now contains three turns equally spaced and positioned from just above the orifice to a point 2/3 down the susceptor. This has resulted in a temperature differential of approximately 40°. A further growth attempt with this arrangement showed most of the past problems with the graphite to be solved. The crucible did not soften and sag and the capillary walls of the die stayed in position with no distortion. The only problem left to resolve with the setup is the maintenance of an adequate gradient at the orifice which will provide even spreading and sustain growth.

This chamber should be large enough for much of our future development needs, but will suffer from many of the drawbacks of other rf heated systems. Resistance furnaces will provide better access, monitoring, and multizone temperature control. While successful EFG was not demonstrated when resistance heating was tried in the past with sapphire, this was largely due to the nature of the heaters needed to reach and operate at a temperature of 2100°C.

Growth experiments will continue in the large system with the main aim of obtaining enough ribbons from a large melt to determine the effects of melt size on purity. Optimization of the growth will take place over the next two months.

C. Die Materials

As reported in the last quarterly, compatibility tests of ZrSiO and $ThSiO_4$ were run by melting Si with quantities of the powdered materials. Tests were conducted with the powders mixed with Si powder and also with solid Si. Initial analysis of these tests using Debye-Scherrer X-ray photographs as reported before was encouraging. Further work was done with these samples during this period.

Qualitative spectrographic analyses of the last-to-freeze portions of the silicon melts held in contact with the $ZrSiO_4$ and $ThSiO_4$ have shown significant contamination of the Si by both materials. Both metals, Zr and Th, were found to be present in concentrations of the order of 1%. The choice of the last-to-freeze part of the melt was deliberate, in that this part of the melt would contain the highest impurity concentration due to rejection of impurity atoms from the previously solidified material. Also, this part of the melt, since it is extruded from the interior of the solidifying melt (due to silicon's expansion on freezing), is least apt to be contaminated by particles of the powdered silicate material which would give a misleadingly high concentration of the refractory metal. These results would seem to

eliminate the refractory silicates from further consideration for direct use as die materials. However, as a further check on the analyses, EFG or Czochralski growth from a melt in contact with one of the silicates is necessary.

Hot-pressed mixtures of quartz and graphite containing 1% and 0.3% graphite have been fabricated and tested for wettability. Both show contact angles less than 90°. The 1% material is about 65° and the 0.3% material is about 82°. Thus, we have seen, from 3.0% to 0.3%, the contact angle follow the concentration of graphite in a regular fashion. These current materials are both presently being fabricated into dies for testing.

IV. ACKNOWLEDGEMENTS

We acknowledge the kind assistance of Dr. Ogden Marsh, Hughes Research Laboratories, Malibu, California, for measurement of carrier mobilities and concentrations and Dr. Leon Crossman and Mr. John A. Baker of Dow-Corning Corporation, Semiconductor Products Division for their measurements of impurity concentrations in our silicon ribbons.

V. NEW TECHNOLOGY

No new technology disclosures are to be reported during this contracting period.

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VI. CONCLUSIONS AND RECOMMENDATIONS

We have seen some improvements in the electrical quality of our ribbon as shown by improved solar cell results. These results appear due to improved handling techniques and setup preparation methods. The use of the laminar flow bench, vacuum bakeout, DFP-2 graphite and new fabrication techniques have all contributed in this area. More work will be done to determine whether these methods and newer ones to be tried are all necessary to guarantee the best material.

The wetting tests with the quartz carbon mixtures have shown the feasibility of these materials for use as dies. Dies are being fabricated and growth will be made with this material in the near future. The wetting tests with the silicates have shown them to be unsuitable for silicon growth die materials.

The scaled-up system is assembled and emphasis will be placed on producing ribbons from the apparatus.

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